Novel Polymer Composite Coating on Mildsteel Substrate for Corrosion Resistance

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ABSTRACT

The polymer – ceramic composites have superior characteristics and play vital role in various applications. In the present study, a polymer – ceramic composite is developed using the high molecular weight PMMA and zirconium titanate. While the former is prepared by the polymerization of MMA , the latter is prepared by sol gel method. The composite samples are characterized using DSC,PXRD, and SEM. The high Tg values of polymer composite show the restricted segmental motions of the polymer chains at the organic / inorganic interface. The PXRD data ensures the distribution of zirconium into the polymer. The rough fractured surface of PMMA is altered due to the incorporation of zirconium titanate into the polymer. The polymer-ceramic composite is coated over mild steel substrate and the corrosion resistance behaviour is studied.

Keywords: Polymer composite, PMMA, Zirconium titanate, corrosion resistance.

1. INTRODUCTION

Composites are materials obtained by bonding two or more materials together. The characteristics of the resulting materials are not that of the components in solution. Advanced composites of low weight can be substitutes for metallic parts. Application of polymer composites as engineering materials has become the state of the art. These composite materials nowadays play an increasingly important role due essentially to their lighter weight and better corrosion resistance. These materials usually comprise of a polymer matrix in which fibers and/or smaller filler particles are thoroughly dispersed[1]. The filler must be well dispersed in the matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing[2]. Corrosion is the deterioration of materials by chemical interaction with their environment. All corrosion reactions are electrochemical in nature consisting of anodic and cathodic

sites. At the anodic site, dissolution of the metal takes effect leading to the release of electrons whereas at the cathodic site, the electrons react with some reducible component of the electrolyte and they are removed from the metal. Various surface techniques have been developed to improve the corrosion resistance of metals. Among the several methods of corrosion control such cathodic protection[3,4], anodic protection[5], coating[6] and alloying. One of the most effective methods is to deposit protective polymer – ceramic coating on the metal surface[7]. Sol gel ceramic coatings have been extensively employed for the wear, corrosion and oxidation protection of metals[8].

Corrosion is a serious environmental problem in the oil, fertilizer, metallurgical and other industries[9]**.** Valuable metals, such as mild steel, aluminum, copper and zinc are prone to corrosion when they are exposed to aggressive media such as, acids, bases and salts[10]. Therefore, there is a need to protect these metals against corrosion. Polymers find applications as effective corrosion inhibitors for steel[11]. The use of polymers as corrosion inhibitors have drawn considerable attention recently due to their inherent stability and cost effectiveness. Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared to their monomer analogues[12]. Hence, it is expected that the polymers will be better corrosion inhibitors. Polymers such as polyethylenimine and polyvinylpyrrolidone, poly (o-phenylenediamine), polyanthranilic acid, polyacrylic acid, polyvinyl pyridine and polyvinylpyrrolidone, maleic anhydride and N-vinyl-2-pyrrolidone, polyamino-benzoquinone, polyvinyl alcohol, and polyethylene glycol have been reported[13]. PMMA/flaky aluminium composite particle was prepared in the presence of MPS by means of in situ emulsion polymerization of MMA, in order to enhance corrosion resistance of aluminium pigments[14].

In continuation of our quest for developing anti corrosion agent with high effectiveness and efficiency, the present paper aims at the utilization of PMMA/ZT composite as anti corrosion agent. It is characterized by potentiodynamic polarization and electrochemical impedance spectroscopy.

2. EXPERIMENTAL

Materials

The monomer MMA, zirconium titanate, benzoyl peroxide, chloroform and petroleum ether were obtained from SD Fine Chemicals Limited, Mumbai, India.

Preparation of Zirconium titanate

Zirconium oxychloride and Oxalic acid were mixed to get a white floc, followed by solution formation. TiO_2 was added to the solution and stirred. After stirring, MgO and Fe_2O_3 were added and again subjected to stirring and a mixed solution was formed. The solution formed was converted into a gel, dried at 45^o C and calcined at 1200^o C. As a result a fine powder of $ZrTiO_4$ was obtained.

Preparation of PMMA/ZT composite

Polymer composite samples (PMZT 1 and 2) were prepared as follows:

Calculated quantities of PMMA were dissolved in chloroform followed by the addition of calculated quantities of zirconium titanate and then made into a paste in an agate mortar. The resulting mixture was subjected to heat at 120°C for 24 hours in a Muffle furnace and made into a powder[15].

Coating of mild steel substrates with polymer composites

The mild steel plates of 1 square cm area were polished with emery paper and immersed in 10% dilute sulphuric acid for 30 minutes and then the plates were washed with distilled water and rinsed with acetone. PMMA was dissolved in chlorofom. Zirconium titanate was added to this solution with stirring followed by the addition of PVA. The surface treated mild steel panel was then immersed in the above mixture for coating and kept at 110°C for 6 hours. The corrosion studies were performed in a classical three electrode electrochemical cell. The coated mild steel plates were subjected to Potentiodynamic and EIS polarization measurements. The corrosion resistance behavior of the coated polymer-ceramic composite samples was studied using electrochemical tests (Polarization and Impedance measurements). The polarization curves for the prepared coatings were obtained in 3.5% NaCl solution using Autolab Potentiostat electrochemical measurement system.

3. RESULTS AND DISCUSSION

Characterization

Thermal behavior

The DSC spectrums of PMMA, PMZT 1 and PMZT 2 were recorded using Netsch DSC 204. The glass transition temperature (T_g) of pure polymer PMMA, polymer composite sample 1 and polymer composite sample 2 were found to be 374.4K, 711.24K and 715.01K respectively. (Figures. 1-3). The results indicate that the T_g has been increased from 374 to 711K (fig.1 and2). The improvement in the T_g for sample 1 is due to the fact that polymer composite has a high aspect ratio in the PMMA matrix and the segmental motions of the polymer chains are restricted at the organic- inorganic interface. Similarly, sample 2 has recorded a further raise in Tg (fig. 3).

Out of the two samples, sample 2 possess a high T_g . Higher concentration of polymer has favoured the increase in T_g value. High rigidity of the polymer composite is due to bulky side groups on the polymer chains resulting in high T_g values. High T_g value has enabled the polymer composite to acquire good strength, high degree of crystallinity and cross linking resulting in high resistance to deformation.

The remarkable difference in the glass transition temperatures of the polymer and the composites has an impact on the structural as well as dynamic properties of these materials.

The value of C_p for the pure polymer was found to be 0.715 J/gK^{-1} for polymer composite sample 1 it was found to be - 392.09 J/gK^{-1} and for polymer composite sample 2 it was found to be – 220.27 J/gK^{-1}.

The delta C_p value for the polymer exhibits the exothermic nature of the

polymer,where as the composite samples 1 and 2 exhibit themselves as endothermic.

PXRD

In order to understand the properties of composite material, it is essential to know about the details of its structure. Diffraction techniques were adapted to characterize the synthesized composites. The X-ray diffraction pattern (XRD) technique was used for characterization.

The PXRD of PMMA, zirconium titanate, PMZT 1 and PMZT 2 were recorded using X'PERT PRO diffractometer. The XRD peaks of the PMMA, zirconium titanate and the composites were shown in the figure 4. The XRD analysis of PMZT 1 and PMZT 2 showed a similar pattern. While analyzing the composite peaks, the intensities of the precursor peaks were not reflected. At the same time, the positions of few peaks in the composites have been shifted compared to zirconium titanate peaks.

SEM

The SEM images of PMMA, PMZT 1 and PMZT 2 are shown in the figures 5(a), (b) and (c) respectively.

Coating Characterization

PXRD

The XRD of PMZT 1 coated mild steel, PMZT 2 coated mild steel and Bare mild steel were recorded using X'PERT PRO diffractometer (figures 6, 7, and 8). Polymer – ceramic composite coating on mild steel substrate is ensured by XRD.

Electrochemical measurements

The values of corrosion potential and corrosion current of Bare mild steel, PMZT 1 coated mild steel and PMZT 2 coated mild steel are shown in Table 1. When compared to bare mild steel substrate, the polymer – ceramic composite coated mild steel substrates exhibit lower values of Ecorr and Icorr which indicate better corrosion resistance. From the results (Tafel), it is observed that PMZT 1 coated mild steel is having higher corrosion resistance than PMZT 2 coated mild steel. This is because of higher proportion of zirconium titanate (polymer to ceramic composition 1:1) in the coated polymer - ceramic – composite substrate. Therefore higher proportion of zirconium titanate in the coating favours corrosion resistance.

Nyquist and Bode plots of Bare mild steel, PMZT 1 coated mild steel and PMZT 2 coated mild steel are shown in the figures 11-16. The Nyquist plots illustrate that the mild steel plates coated with polymer – ceramic composite samples 1 and 2 show an excellent corrosion resistance compared to the bare mild steel substrate (Table 1). The results are in accordance with those of polarization curves.

Table.1. Corrosion kinetic parameter of bare mild steel and polymer composite samples

Corrosion parameter	Sample		
	Bare-mild steel	PMZT 1 coated on Mild steel	PMZT 2 coated on Mild steel
E_{corr}, mV	-822.167	-544.607	-649.953
I_{corr}, µA	8.699	2.401	4.312
Corrosion Rate, mmpy	0.2408140	0.0664668	0.1193690

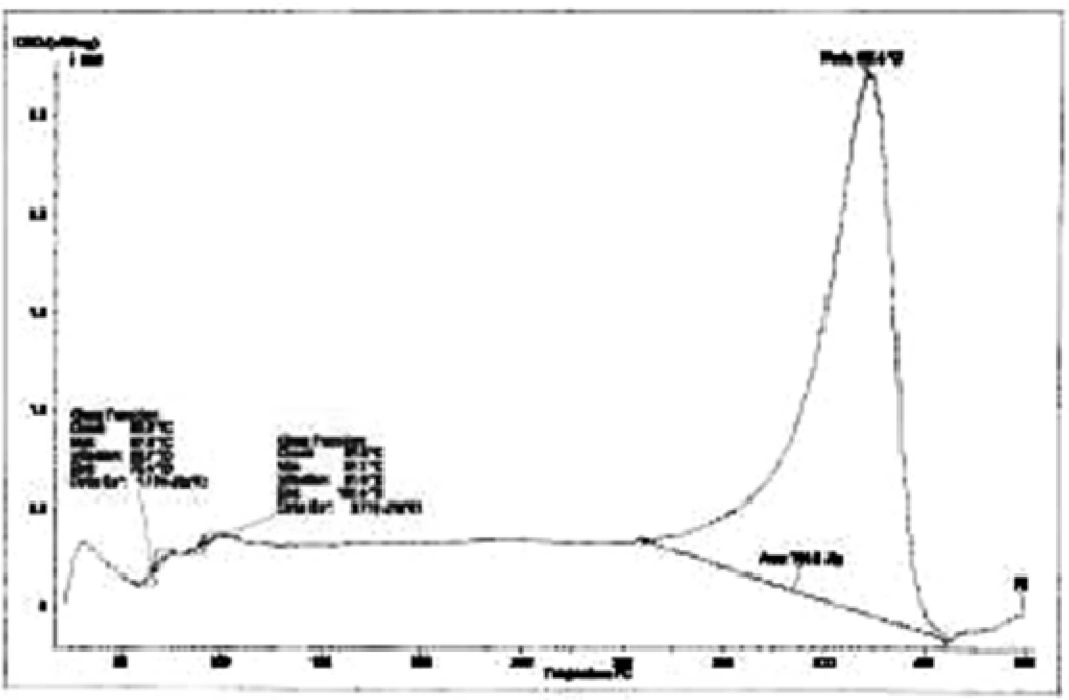


Figure.1. DSC of PMMA

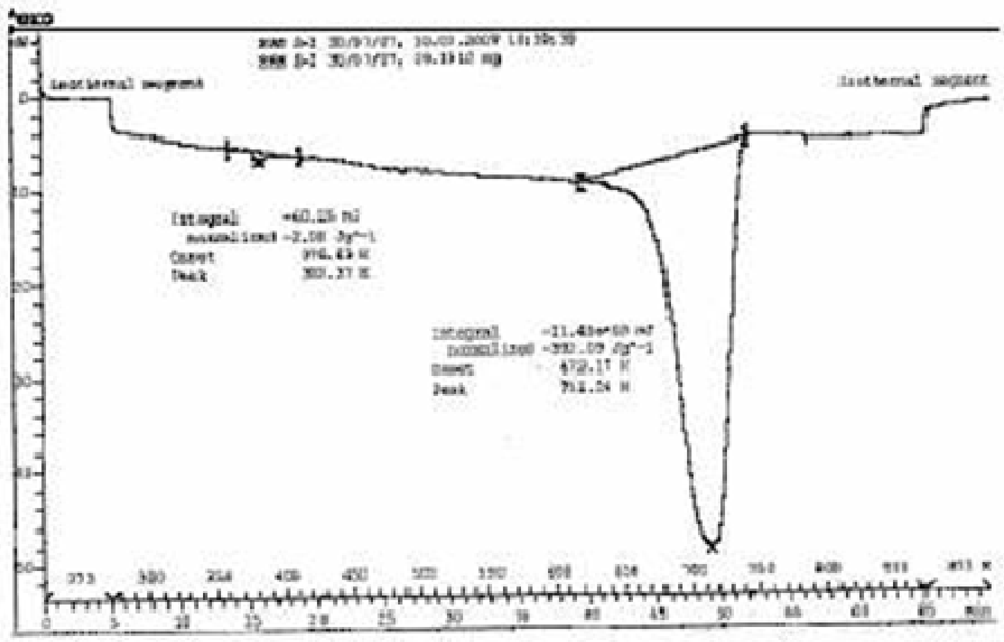


Figure.2. DSC of PMZT 1

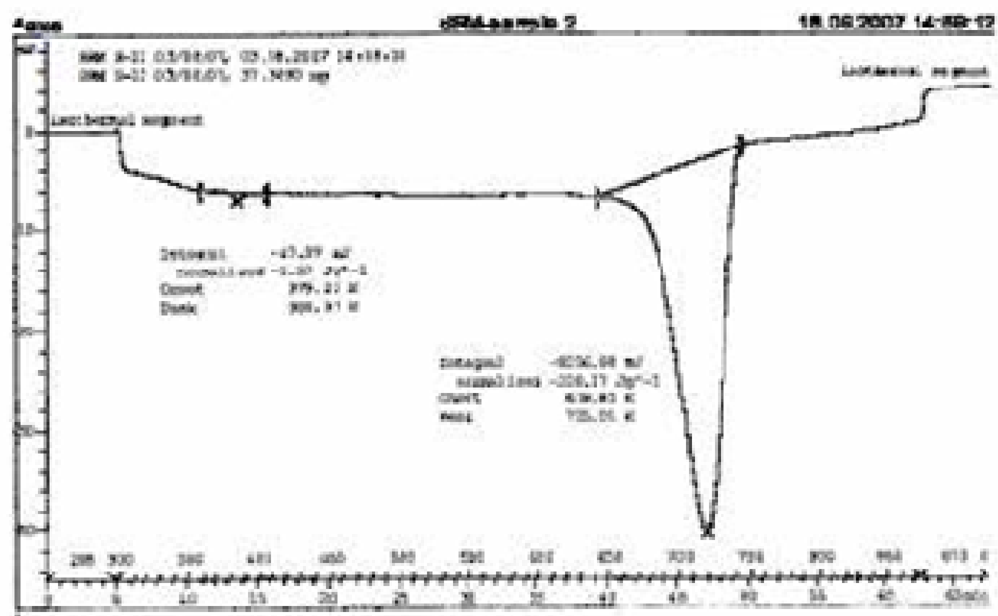


Figure.3. DSC of PMZT 2

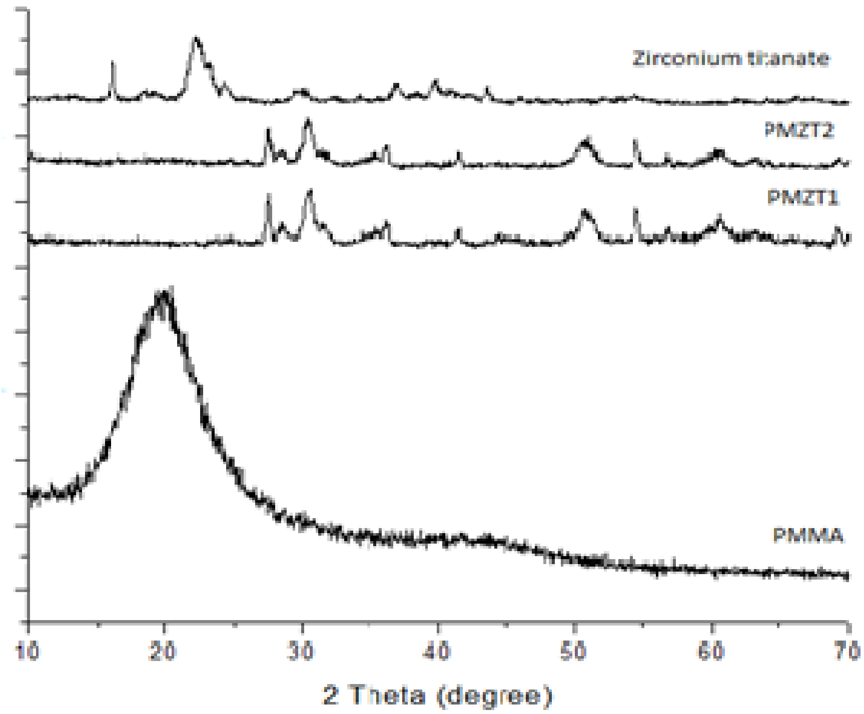
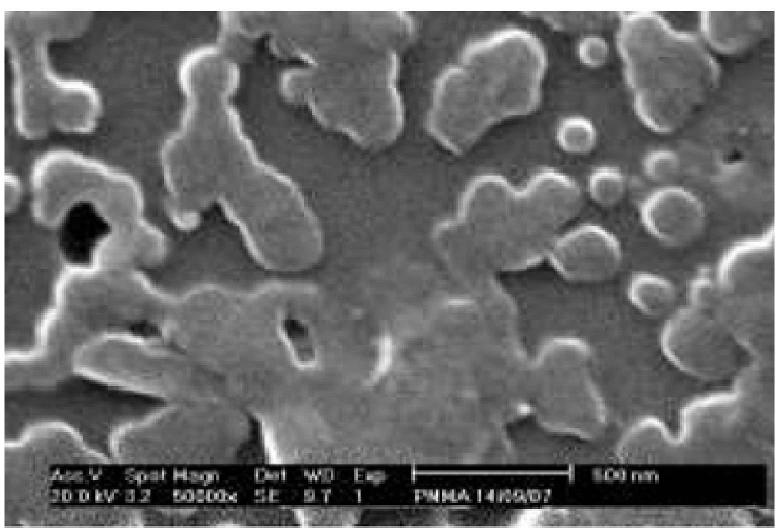
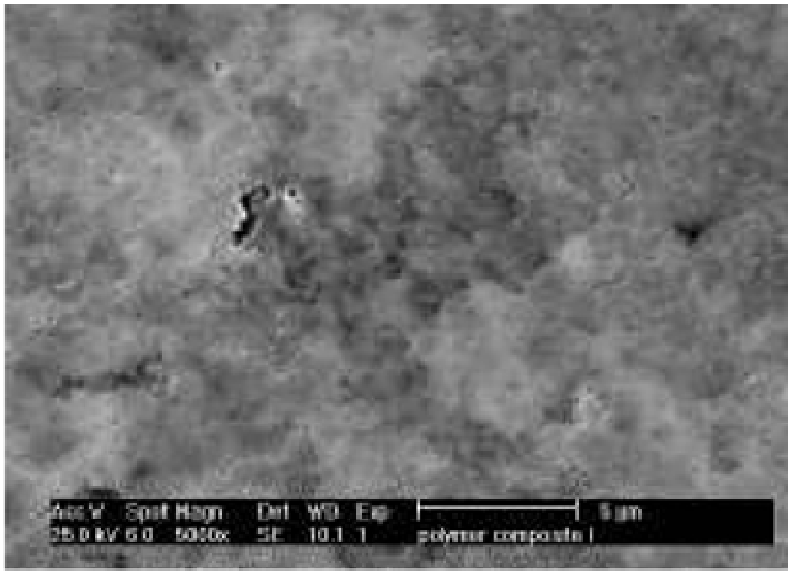


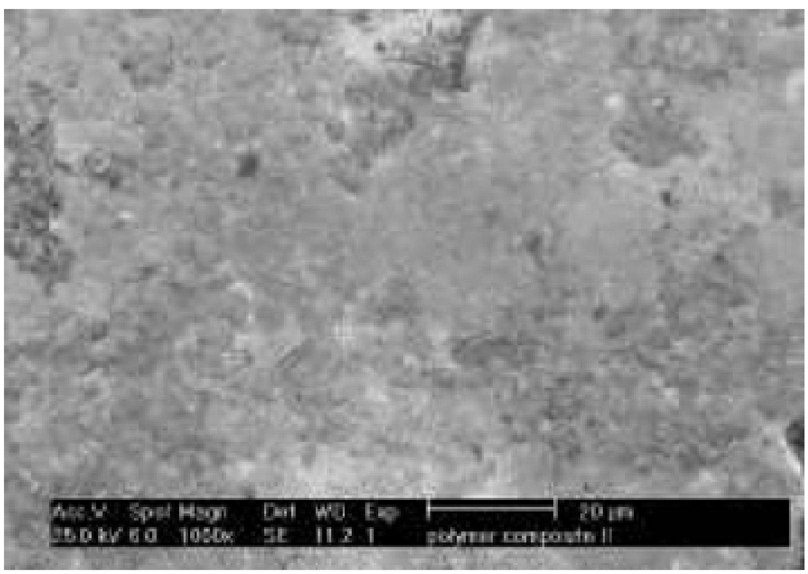
Figure.4. XRD patterns of PMMA, PMZT 1, PMZT 2 and ZT



(a)



(b)



(c)

Figure.5. (a, b, c) SEM images of PMMA, PMZT 1 and PMZT 2

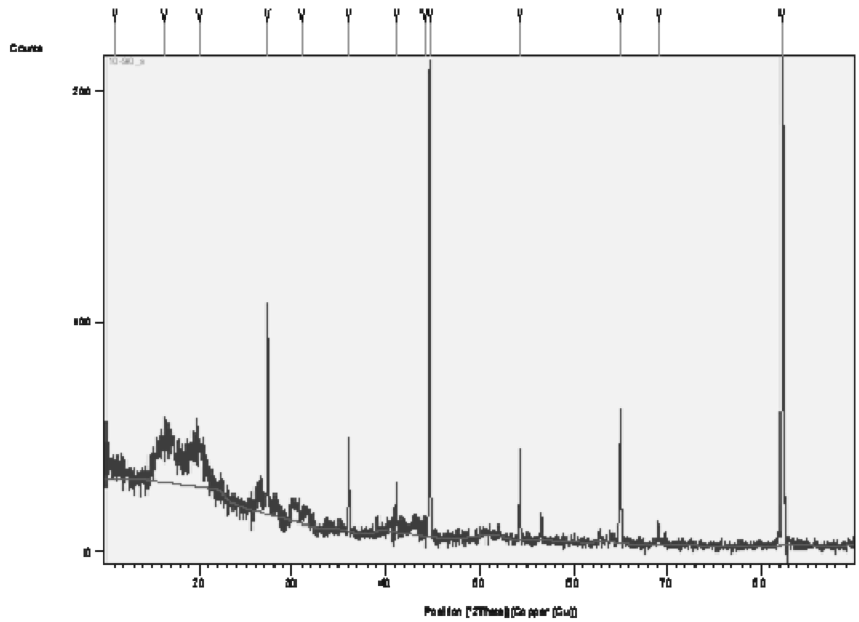


Figure. 6. XRD of Mild Steel Coated with PMZT 1

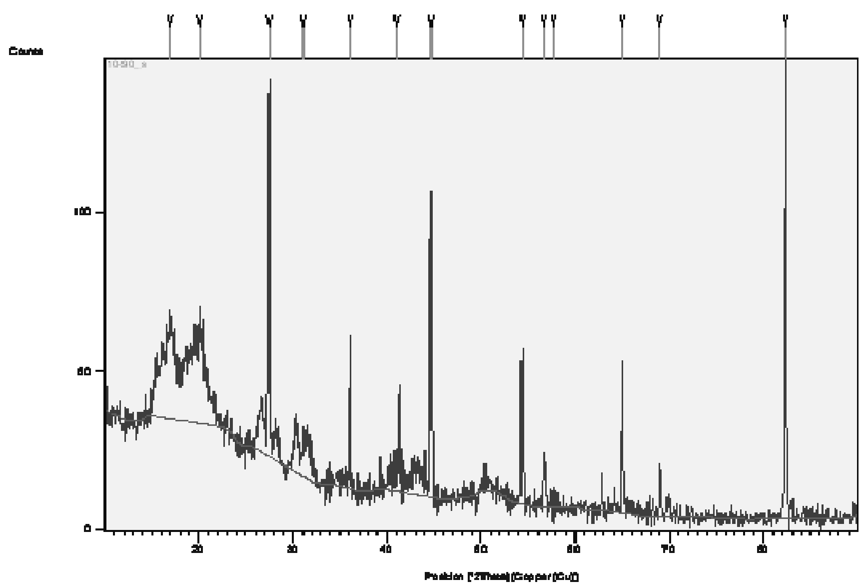


Figure. 7. XRD of Mild Steel Coated with PMZT 2

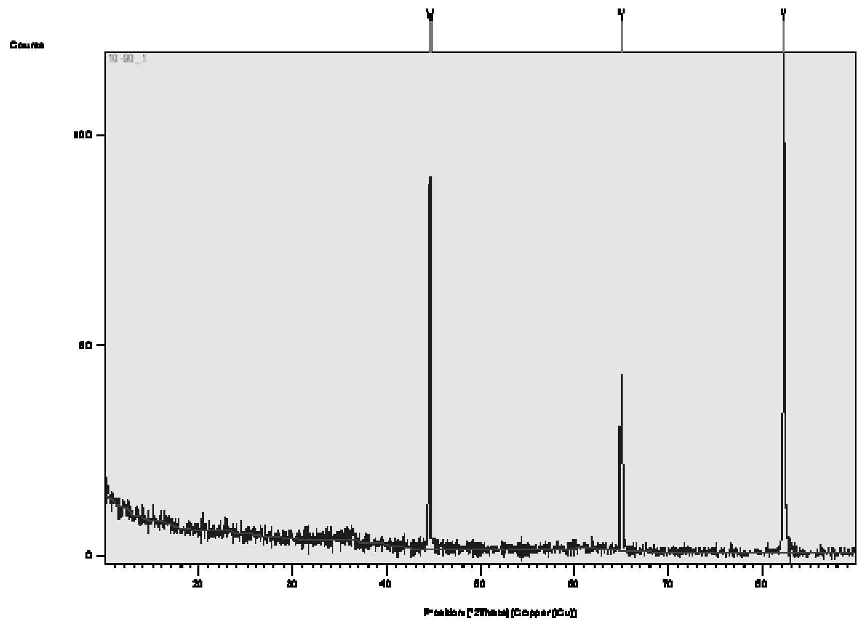


Figure. 8. XRD of Bare mild Steel

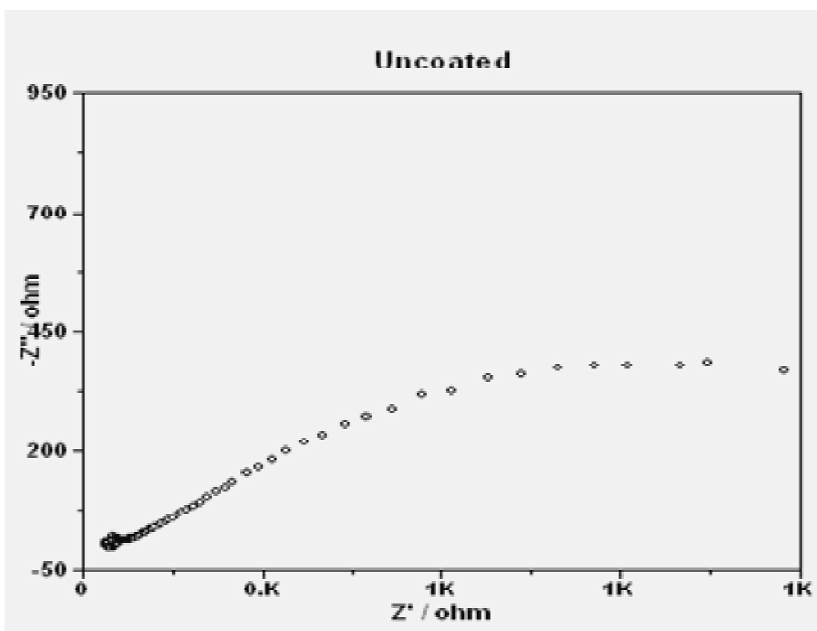


Figure. 9. NYQUIST PLOT of Bare mild Steel

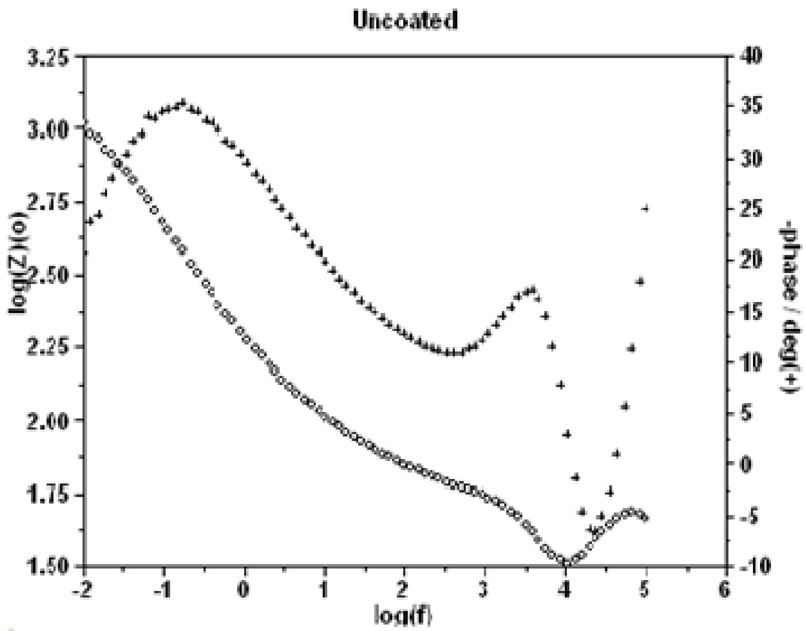


Figure.10. BODE PLOT of Bare mild Steel

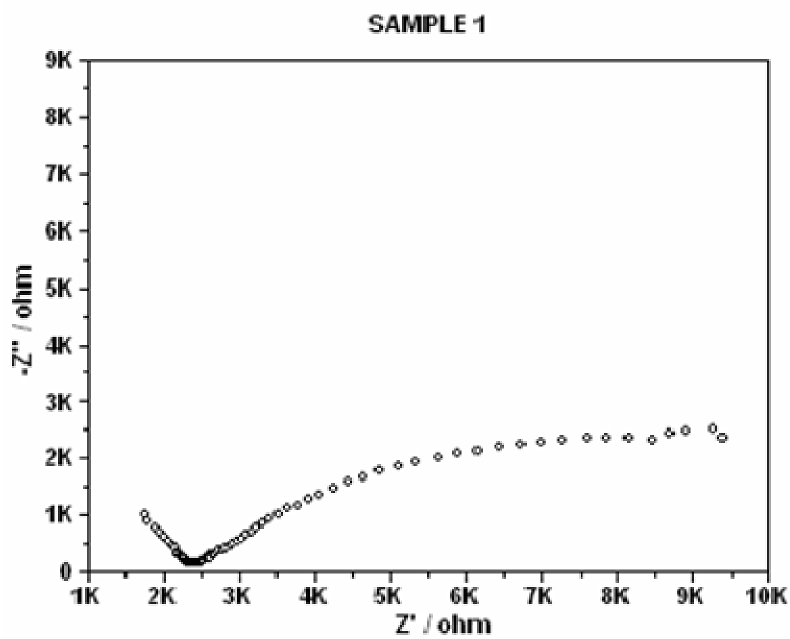


Figure. 11. NYQUIST PLOT OF PMZT 1(Coated Mild Steel)

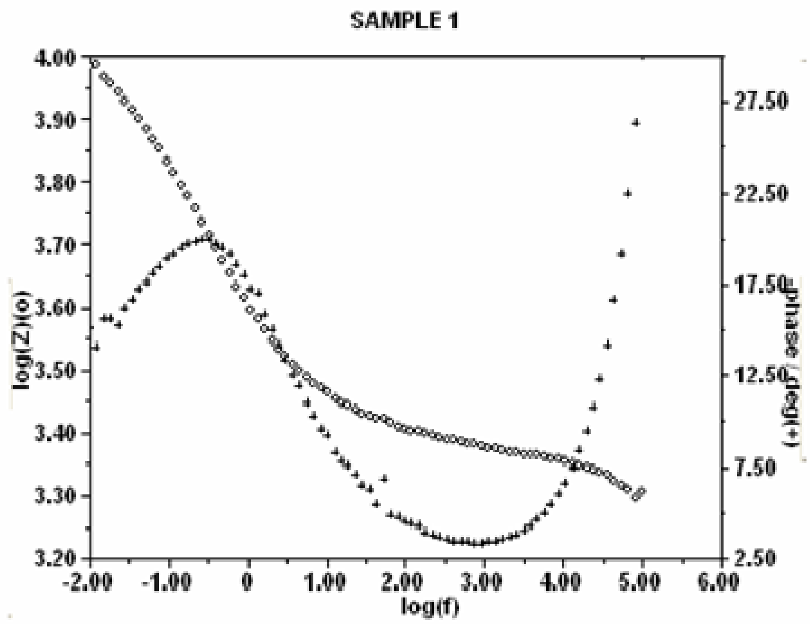


Figure.12. BODE PLOT OF PMZT 1(Coated Mild Steel)

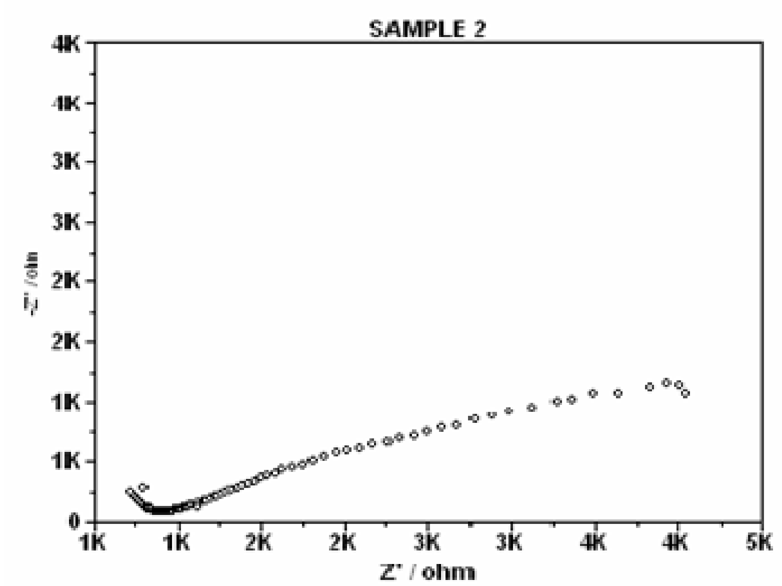


Figure. 13. NYQUIST PLOT OF PMZT 2(Coated Mild Steel)

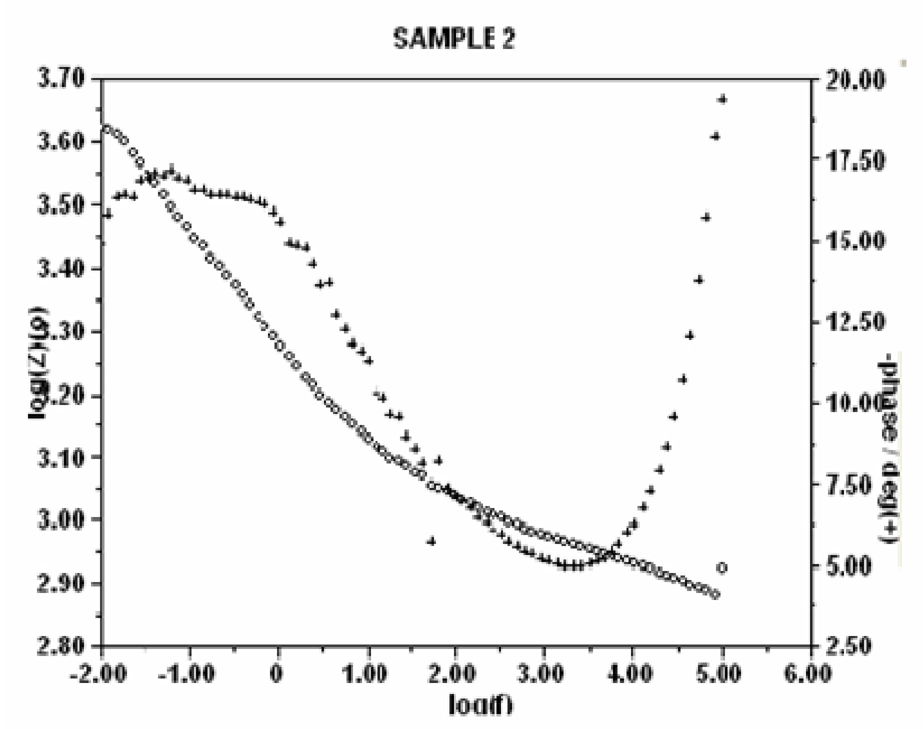


Figure. 14. NYQUIST PLOT OF PMZT 2(Coated Mild Steel)

4. CONCLUSION

The thermal stability of polymer composite was improved by the addition of zirconium titanate. The incorporation of PMMA in zirconium titanate results in materials possessing high strength and thermal stability. The polymer composites are inhomogenous and anisotropic. Without the use of composites the commercial viability of future civil aircraft would be in doubt and it has taken many years, and some failures, to get to the high usage levels of today. PMMA based composite has been developed and the experimental results are evaluated. The composite formation was confirmed by PXRD. From the polarization and electrochemical impedance results, it is well established that the polymer-ceramic composite coated samples have higher corrosion resistance. Hence, the coating of these composites over mild steel can function against corrosion**.**

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